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SPHERICAL BARIUM TITANATE-BASED SEMICONDUCTOR CERAMIC MATERIAL
POWDER AND MANUFACTURING METHOD THEREOF

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[Attached amendments have been incorporated into the text of the translation.]

Abstract

Constitution

A type of spherical barium titanate-based semiconductor ceramic material powder characterized by the fact that it contains a trivalent semiconductor-forming element or pentavalent semiconductor-forming element in an amount of 0.05-2 atom% with respect to titanium, its base material portion is represented by $ATiO_3$ (where A represents: $Ba \geq 50 \text{ atom\%}$, $0 \text{ atom\%} \leq Sr, Ca, Pb \leq 50 \text{ atom\%}$), and it has a grain diameter in the range of 0.3-50 μm .

Effects

For said spherical barium titanate-based semiconductor ceramic material powder, the grain diameter can be controlled at will; the grain size distribution is narrow; the dispersion property is good; and the grain size is uniform, so that it can be used in manufacturing semiconductor ceramic material with excellent resistivity versus temperature characteristics, etc.

Claims

1. A type of spherical barium titanate-based semiconductor ceramic material powder characterized by the fact that it contains a trivalent semiconductor-forming element or pentavalent semiconductor-forming element in an amount of 0.05-2 atom% with respect to titanium; its base material portion is represented by $ATiO_3$ (where A represents: $Ba \geq 50 \text{ atom\%}$, $0 \text{ atom\%} \leq Sr, Ca, Pb \leq 50 \text{ atom\%}$), and it has a grain diameter in the range of 0.3-50 μm .
2. The spherical barium titanate-based semiconductor ceramic material powder described in Claim 1, characterized by the fact that $ATiO_3$ is $BaTiO_3$.

3. A type of spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-50 μm , prepared by baking the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1 at 300-1200°C.

4. A method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1 with grain diameter in the range of 0.3-5 μm , characterized by the fact that hydrogen peroxide and a semiconductor-forming agent are present in the wet reaction of a titanium compound and a barium compound, or in the wet reaction of a titanium compound, a barium compound, and a strontium compound.

5. A method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1, characterized by the fact that hydrogen peroxide, semiconductor-forming agent, as well as at least one selected from strontium titanate with grain diameter of 0.2 μm or smaller, calcium titanate with grain diameter of 0.2 μm or smaller, and lead titanate with grain diameter of 0.2 μm or smaller are present in the wet reaction of a titanium compound and a barium compound, or in the wet reaction of a titanium compound, a barium compound, and a strontium compound.

6. The method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 4 or 5, characterized by the following facts: said titanium compound is titanium hydroxide containing a semiconductor-forming element or titanium oxide containing a semiconductor-forming element; said barium compound is barium hydroxide; and, before the reaction of said titanium compound and barium compound, a reaction with hydrogen peroxide is performed for said titanium hydroxide containing a semiconductor-forming element or said titanium oxide containing a semiconductor-forming element.

7. The method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 4 or 5, characterized by the following facts: said titanium compound is titanium hydroxide containing a semiconductor-forming element or titanium oxide containing a semiconductor-forming element; said barium compound is barium hydroxide; said strontium compound is strontium hydroxide; and, before the reaction of said titanium compound, barium compound, and strontium compound, a reaction with hydrogen peroxide is performed for said titanium hydroxide containing a semiconductor-forming element or said titanium oxide containing a semiconductor-forming element.

8. The method for manufacturing barium titanate-based semiconductor ceramic material powder described in Claim 4 or 5, characterized by the fact that the aging reaction of said titanium compound and barium compound or the aging reaction of said titanium compound, barium compound, and strontium compound is carried out at 40-100°C for at least 30 min.

9. A method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1 with grain diameter in the range of 5-50 μm , characterized by the fact that a semiconductor-forming agent is present in the wet reaction of said titanium compound and barium compound or in the wet reaction of said titanium compound, barium compound, and strontium compound, and, after the reaction, it is dried in a gas flow to form said spherical barium titanate-based semiconductor ceramic material powder.

10. A method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1 with grain diameter in the range of 5-50 μm , characterized by the fact that a semiconductor-forming agent and hydrogen peroxide are present in the wet reaction of said titanium compound and barium compound or in the wet reaction of said titanium compound, barium compound, and strontium compound, and, after the reaction, it is dried in a gas flow.

11. A method for manufacturing the spherical barium titanate-based semiconductor ceramic material powder described in Claim 1 with grain diameter in the range of 5-50 μm , characterized by the fact that a semiconductor-forming agent as well as at least one selected from the group of strontium titanate with grain diameter of 0.2 μm or smaller, calcium titanate with grain diameter of 0.2 μm or smaller, and lead titanate with grain diameter of 0.2 μm or smaller are present in the wet reaction of said titanium compound and barium compound or in the wet reaction of said titanium compound, barium compound, and strontium compound, and, after the reaction, it is dried in a gas flow.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a type of spherical barium titanate-based semiconductor ceramic material powder for use in making PTC thermistors, semiconductor capacitors, and other semiconductor ceramic materials.

[0002]

Prior art

For PTC thermistors, in order to ensure a low room-temperature resistivity, a high resistance variation rate, and a high mechanical strength, it is required that grain size be uniform, and the grain boundary thickness be uniform.

[0003]

Also, in order for semiconductor capacitors to have a large dielectric constant, a low dielectric loss, a high voltage rating, and a high mechanical strength, it is required that the grain size be uniform, and the grain boundary thickness be uniform.

[0004]

Usually, for said PTC thermistors, semiconductor capacitors, and other semiconductor ceramics, the grain size is controlled in the range from submicron to 50 μm . Consequently, the grain diameter of the material powder used for it should be in the range of 0.3-50 μm , or preferably in the range of 0.5-50 μm , the grain size distribution should be narrow, and the dispersion property should be good.

[0005]

However, for the barium titanate-based semiconductor ceramic material powders manufactured using conventional methods, there is no way to meet the aforementioned requirements well.

[0006]

In the prior art, the barium titanate-based semiconductor ceramic material powder is manufactured in a method in which titanium oxide, barium carbonate, semiconductor-forming element, etc., are mixed to undergo solid-phase reaction.

[0007]

However, since the solid-phase reaction is carried out at a high temperature, the obtained barium titanate-based semiconductor ceramic material powder has a relatively large grain diameter. Consequently, mechanical crushing is carried out to realize the desired grain diameter. However, in this case, there is a large dispersion in the grain diameter, and the grain shape is not uniform. Consequently, dispersion property is poor. When the obtained powder is used in manufacturing PTC thermistors, semiconductor capacitors, etc., since the grain size has a significant [effect on] dispersion, it is impossible to realize excellent electrical characteristics.

[0008]

In order to solve these problems, it has been proposed that the barium titanate-based semiconductor ceramic material powder be manufactured by means of a wet coprecipitation method using an oxalate salt. (For example, see: *Yogyo Kyokai Shi*, 90 (8), 1982.)

[0009]

However, in the aforementioned method, only fine particles of semiconductor ceramic material powder can be obtained. Also, the grain shape is nonuniform, and grains may merge with each other. Due to these disadvantages, it is impossible to obtain a barium titanate-based semiconductor ceramic material powder with grain diameter of 0.3 μm or larger having a narrow grain size distribution and good dispersion property.

[0010]

Japanese Kokai Patent Application No. Hei 2[1990]-289426 described a method for manufacturing barium titanate-based semiconductor ceramic material powder with good aggregating property and with [grain diameter] of 150 μm or larger by crushing using a ball mill or the like before ceramic formation. However, in this method, it is hard to control the degree of crushing, and the grain shape is not uniform. As a result, the dispersion property is poor, and the results are not sufficiently satisfactory.

[0011]

Problems to be solved by the invention

As explained above, for the conventional barium titanate-based semiconductor ceramic material powder, good control of the grain diameter is impossible, and the dispersion property is poor, so that it is impossible to obtain PTC thermistors, semiconductor capacitors, and other semiconductor ceramics with excellent electrical characteristics.

[0012]

The purpose of this invention is to solve the aforementioned problems of the prior art by providing a type of spherical barium titanate-based semiconductor ceramic material powder characterized by the fact that the grain diameter can be well controlled, and it has good dispersion property.

[0013]

Means to solve the problems

In order to realize the aforementioned purpose, the present inventors have performed extensive research. As a result of this research, it was found that when hydrogen peroxide is present in the wet reaction for manufacturing barium titanate-based semiconductor ceramic material powder, it is possible to obtain spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-5 μm and with a narrow grain size distribution. Also, by means of drying in a gas flow after the wet reaction, it is possible to obtain

barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 5-50 μm . In this way, this invention was reached.

[0014]

That is, this invention provides a type of spherical barium titanate-based semiconductor ceramic material powder characterized by the fact that it contains a trivalent semiconductor-forming element or pentavalent semiconductor-forming element in an amount of 0.05-2 atom% with respect to titanium; its base material portion is represented by ATiO_3 (where A represents: $\text{Ba} \geq 50 \text{ atom\%}$, $0 \text{ atom\%} \leq \text{Sr, Ca, Pb} \leq 50 \text{ atom\%}$), and it has a grain diameter in the range of 0.3-50 μm .

[0015]

In said formula, A has the following meaning: A is Ba, or Ba and at least one selected from the group of Sr, and Ca and Pb. The content of Ba is in the range of 50-100 atom%, and the content of Sr, Ca and Pb is in the range of 0-50 atom%. Ba represents barium; Sr represents strontium; Ca represents calcium; and Pb represents lead.

[0016]

In this case, specific examples of the base material portion represented by ATiO_3 of the spherical barium titanate-based semiconductor ceramic material powder of this invention include barium titanate, barium strontium titanate, barium strontium calcium titanate, barium strontium lead titanate, barium strontium calcium lead titanate, barium calcium titanate, barium lead titanate, and barium calcium lead titanate.

[0017]

In a wet reaction of a barium compound and a strontium compound with a titanium compound, a perovskite type compound is formed. On the other hand, in a wet reaction of a calcium compound and a lead compound with a titanium compound, hardly any perovskite compound is formed.

[0018]

Among the compounds represented by said formula ATiO_3 , barium titanate can be obtained in a wet reaction of a titanium compound and barium compound; and barium strontium titanate is usually obtained in a wet reaction of a titanium compound, barium compound and strontium compound.

[0019]

However, a compound containing calcium and lead cannot be obtained in the wet reaction of a calcium compound, lead compound and titanium compound. Consequently, one should add calcium titanate with grain diameter of 0.2 μm or smaller or lead titanate with grain diameter of 0.2 μm or smaller to the wet reaction of a titanium compound and a barium compound, or to the wet reaction of a titanium compound, barium compound and strontium compound.

[0020]

After the wet reaction of a titanium compound, which is prepared by physical mixing of calcium titanate, lead titanate, etc., and a barium compound, or after the wet reaction of a titanium compound, which is prepared by physical mixing of calcium titanate, lead titanate, etc., and a barium compound and a strontium compound, drying and baking are performed to form a compound with a uniform composition.

[0021]

Among samples of the spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-50 μm and containing 0.05-2 atom% of trivalent semiconductor-forming element or pentavalent semiconductor-forming element with respect to titanium, those with relatively small grain size of 0.3-5 μm can be prepared by having hydrogen peroxide present in the wet reaction of a titanium compound and a barium compound in a system containing a semiconductor-forming element, or in the wet reaction of a titanium compound, barium compound and strontium compound (when calcium and lead should be contained [in the obtained ceramic material powder], calcium titanate with grain diameter of 0.2 μm or smaller or lead titanate with grain size of 0.2 μm or smaller is added to said reaction system; or, strontium is introduced by adding strontium titanate; in this case, strontium titanate with grain diameter of 0.2 μm or smaller manufactured separately in a wet reaction is added to said reaction system).

[0022]

It is believed that the reason for this is as follows: compared with the case when there is no hydrogen peroxide, when hydrogen peroxide is present in the reaction for forming the barium titanate-based semiconductor ceramic material powder, the reaction slowed and formation of fine grains in the barium titanate-based semiconductor ceramic material powder is suppressed, so that spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-5 μm and with a narrow grain size distribution is formed.

[0023]

Then, based on the fact that the use of hydrogen peroxide can slow the reaction for forming barium titanate-based semiconductor ceramic material powder as explained above, by changing the reaction conditions of the wet reaction, it is possible to control the grain diameter of the obtained barium titanate-based semiconductor ceramic material powder at will.

[0024]

In addition, among the samples of the spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-50 μm , those with relatively large grain diameter in the range of 5-50 μm can be obtained by drying in a gas flow after said wet reaction.

[0025]

For the spherical barium titanate-based semiconductor ceramic material powder containing 0.05-2 atom% of trivalent semiconductor-forming element or pentavalent semiconductor-forming element with respect to titanium, having base material portion represented by ATiO_3 and having a grain diameter in the range of 0.3-50 μm , the grains literally have a spherical shape, the grain size distribution is narrow, the dispersion property is excellent, and the grain diameter can be controlled at will. Consequently, when the powder is used in forming ceramics, it is possible to obtain PTC thermistors, semiconductor capacitors, and other semiconductor ceramics with desired grain size, little dispersion in the grain size, and excellent electrical characteristics and mechanical characteristics.

[0026]

When said spherical barium titanate-based semiconductor ceramic material powder is baked, the crystal form is changed from pseudocubic system to cubic or tetragonal system, the crystallinity is improved, and the grain size and grain boundary can be better controlled, so that a better semiconductor ceramic material powder is obtained.

[0027]

For the cubic tetragonal barium titanate-based semiconductor ceramic material powder prepared by baking, because the spherical barium titanate-based semiconductor ceramic material powder before baking literally has a spherical shape, with few contact points between grains, there is little sintering in baking, and the grain diameter of the spherical barium titanate-based semiconductor ceramic material powder can be well maintained after baking, so that the grain size distribution is narrow and the dispersion property is excellent.

[0028]

By selecting the appropriate baking temperature, it is also possible to obtain spherical barium titanate-based semiconductor ceramic material powder that is converted to a semiconductor state in powder form.

[0029]

In addition, by increasing the baking temperature, it is possible to obtain a rectangular parallelepiped single crystal with a higher density.

[0030]

In the following, the various structural elements of the spherical barium titanate-based semiconductor ceramic material powder of this invention will be explained.

[0031]

According to this invention, the trivalent semiconductor-forming element or pentavalent semiconductor-forming element may be of any element that can substitute for Ba or Ti in the perovskite structure of barium titanate to display semiconductor property. Examples of such trivalent semiconductor-forming elements and pentavalent semiconductor-forming elements include Nb, Sb, Ta, Bi, B, as well as Y, La, Ce, Pr, Nd, and other rare-earth elements. At least one is selected from this group for use.

[0032]

For said trivalent semiconductor-forming element or pentavalent semiconductor-forming element, the amount is such that the proportion with respect to titanium in the finally formed ATiO_3 is in the range of 0.05-2 atom%. If the trivalent semiconductor-forming element or pentavalent semiconductor-forming element is smaller than the aforementioned range, a sufficient semiconductor property cannot be displayed. On the other hand, if the amount of the trivalent semiconductor-forming element or pentavalent semiconductor-forming element exceeds the aforementioned range, atomic valence compensation takes place, and semiconductor property is not displayed.

[0033]

For the spherical barium titanate-based semiconductor ceramic material powder of this invention, in addition to the semiconductor-forming element, the base material portion is

represented by ATiO_3 . Here, for ATiO_3 , A represents: $\text{Ba} \geq 50 \text{ atom\%}$, $0 \text{ atom\%} \leq \text{Sr, Ca, Pb} \leq 50 \text{ atom\%}$.

[0034]

Here, if Ba is less than 50 atom%, it is impossible to obtain spherical grains in a wet reaction. Sr, Ca, Pb, etc., are added to change the start temperature to change the resistance of PTC thermistors or to control the sintering temperature and dielectric characteristics of semiconductor capacitors.

[0035]

In the following, the reaction materials will be explained. As mentioned above, in the wet reaction of a barium compound and a strontium compound with a titanium compound, a perovskite compound is formed. On the other hand, in the wet reaction of a calcium compound and a lead compound with a titanium compound, hardly any perovskite compound can be formed. In the wet reaction of a barium compound and a strontium compound with a titanium compound, even when a calcium compound and a lead compound are added, a perovskite compound is still not formed.

[0036]

Consequently, the following method is used: when calcium and lead are to be contained in the spherical barium titanate-based semiconductor ceramic material powder, calcium titanate or lead titanate manufactured in a solid-phase reaction are crushed as needed to a grain diameter of 0.2 μm or smaller. They are then added to the wet reaction of said barium compound, strontium compound, and titanium compound, and, when barium titanate grains or barium strontium titanate grains are formed as spherical aggregates, said calcium titanate or lead titanate is uniformly dispersed in the spherical aggregates.

[0037]

By adding strontium titanate with a grain diameter of 0.2 μm or smaller to the wet reaction of said barium compound and titanium compound, strontium may also be contained in the spherical barium titanate-based semiconductor ceramic material powder.

[0038]

As explained above, a semiconductor-forming element may also be contained beforehand in the calcium titanate, lead titanate, strontium titanate, etc., to be added to the reaction system.

[0039]

According to this invention, for the added calcium titanate, lead titanate, strontium titanate, etc., the grain diameter should be 0.2 μm . This is because if the grain size is larger than 0.2 μm , dispersion of the various additive grains in the aggregates of barium titanate grains or barium strontium titanate grains becomes nonuniform, it becomes difficult to form spherical grains, and diffusion of the additive grains during baking or ceramic formation becomes insufficient, so that it is impossible to obtain a product with a homogeneous composition.

[0040]

According to this invention, there is no special limitation on the type of titanium compound, as long as it can react with the barium compound to form a perovskite-type barium titanate. However, it is preferred that it be partially or completely soluble in the aqueous hydrogen peroxide solution. Especially, it is preferred that no degradation in characteristics take place even when it is mixed in the barium titanate formed.

[0041]

From this viewpoint, examples of preferable titanium compounds include titanium oxide, titanium hydroxide, and other inorganic titanium compounds, as well as titanium oxalate, titanium alkoxide, and other organic titanium compounds.

[0042]

Usually, said titanium hydroxide can be prepared by hydrolysis of an aqueous solution of titanium alkoxide or titanium salt. On the other hand, titanium oxide can be prepared by wet heating of titanium hydroxide or thermal hydrolysis of a titanium salt.

[0043]

As a preferable method for adding the semiconductor-forming element, a prescribed amount of the semiconductor-forming agent (a compound of a semiconductor-forming element which can generate the semiconductor-forming element by means of hydrolysis or the like) is added and dissolved in the titanium solution before hydrolysis. That is, because the semiconductor-forming agent is added to the titanium solution, at the same time as hydrolysis of the titanium solution, hydrolysis also occurs for the semiconductor-forming agent (that is, simultaneous precipitation takes place at the pH for simultaneous hydrolysis of the semiconductor-forming element and hydrolysis of titanium) to form titanium hydroxide containing the semiconductor-forming element or titanium oxide containing the semiconductor-forming element, so that the semiconductor-forming element is dispersed

uniformly in the finally formed spherical barium titanate-based semiconductor ceramic material powder.

[0044]

There is no special limitation on the type of the barium compound as long as it can react with said titanium compound to form a perovskite-type barium titanate. Usually, however, a basic barium compound is used.

[0045]

It is preferred that components that degrade the characteristics as they are mixed in the formed barium titanate are prevented from being mixed in with it. From this viewpoint, the preferable barium compounds include barium hydroxide, barium oxide, barium alkoxide, etc.

[0046]

Just as for said barium compound, for the strontium compound, too, there is no special limitation on the type as long as it can react with the titanium compound to form a perovskite-type strontium titanate. Usually, however, a basic strontium compound is used. Examples of preferable strontium compounds include strontium hydroxide, strontium oxide, strontium alkoxide, etc.

[0047]

There is no special limitation on the type of hydrogen peroxide. However, in order to facilitate use, usually the following types of hydrogen peroxide are used: the commercially available 30% (wt%, same in the following) aqueous solution of hydrogen peroxide, 35% aqueous solution of hydrogen peroxide, 50% aqueous solution of hydrogen peroxide, and 60% aqueous solution of hydrogen peroxide.

[0048]

In the following, the reaction method will be explained. When the strontium compound is used, it can be handled in almost the same way as the barium compound, therefore, an explanation will not be repeated, except the portions unique to the strontium compound. In the explanation, it is assumed that a semiconductor-forming element is contained in the titanium compound beforehand. However, in the practical case, addition of the semiconductor-forming element is not limited to this case. It may also be added to the wet reaction of a titanium compound and a barium compound. Also, it may be added to the barium compound.

[0049]

There is no special limitation on the order of reaction of said titanium compound, barium compound, and hydrogen peroxide, except when reaction is performed at a low concentration. Then it is preferred that the titanium compound and hydrogen peroxide be mixed for reaction before adding the barium compound. The reason is as follows: except for a reaction at a low concentration, if hydrogen peroxide is added to a system containing a barium compound, little soluble barium peroxide (BaO_2) is formed as precipitation, and it becomes irrelevant to the reaction.

[0050]

As far as the amount of hydrogen peroxide is concerned, the molar ratio of hydrogen peroxide to titanium compound (converted to titanium oxide equivalent), that is, $\text{H}_2\text{O}_2/\text{TiO}_2$ (molar ratio), is preferably in the range of 0.1-10.

[0051]

When hydrogen peroxide reacts with a titanium compound that forms little peroxide, the amount of peroxide formed is small. Consequently, when the amount of peroxide formed is to be increased, it is necessary to use an excess amount of [hydrogen peroxide]. Consequently, although the amount of hydrogen peroxide may be excessive with respect to the titanium compound, if the molar ratio of hydrogen peroxide to titanium compound is over 10, the effect levels off, and it merely decomposes in the reaction with the titanium compound. This is undesired economy-wise. On the other hand, if the amount of hydrogen peroxide is such that said molar ratio is smaller than 0.1, addition of hydrogen peroxide cannot sufficiently display its effect.

[0052]

When a titanium compound and hydrogen peroxide are mixed with each other to undergo reaction, titanium peroxide is formed, and usually a yellow sol-like solution is formed.

[0053]

Mixing of hydrogen peroxide may be carried out at room temperature. However, in order to facilitate generation of titanium peroxide and to remove the residual hydrogen peroxide in as short a time as possible, it should be heated at 40-100°C, or preferably in the range of 70-100°C.

[0054]

When the barium compound is added, the titanium oxide equivalent concentration of the titanium compound should be in the range of 0.01-2.5 mol/L, or preferably in the range of 0.06-1 mol/L. If said concentration is over 2.5 mol/L, the viscosity rises and it becomes harder to agitate. For the barium titanate-based semiconductor ceramic material powder obtained in the reaction with a barium compound, the grain diameter becomes nonuniform. If said concentration is lower than 0.01 mol/L, the reactivity decreases significantly.

[0055]

The barium compound is added to said solution of titanium peroxide and mixed uniformly for reaction, with the ratio of barium to titanium, that is, Ba/Ti (atomic ratio) being in the range of 0.8-10, or preferably in the range of 1-3.

[0056]

In this case, the titanium compound and barium compound react to form a pseudocubic perovskite-type barium titanate-based semiconductor ceramic material powder. In order to form a spherical barium titanate-based semiconductor ceramic material powder of 0.3-5 μm , it is preferred that the atomic ratio of titanium and barium, the concentration of barium compound, reaction temperature, etc., be set such that the reaction for forming the barium titanate-based semiconductor ceramic material powder does not end within 1 h, or preferably does not end within 4 h.

[0057]

In order to ensure that the obtained spherical barium titanate-based semiconductor ceramic material powder has a uniform grain diameter and a narrow grain size distribution, it is preferred that mixing of the titanium compound and barium compound be performed at a temperature lower than the reaction start temperature.

[0058]

In addition, it is preferred that an aging reaction be performed for 0.1 h or longer, or preferably for 1 h or longer at a temperature in a range between the temperature at which said reaction of the titanium compound and barium compound would come to an end in 4 h and the temperature lower than said temperature by 50°C, or more preferably at a temperature in a range between the temperature at which said reaction would come to an end in 4 h and the temperature lower than said temperature by 40°C. Then, after the aging reaction, it is preferred that reaction be performed at a temperature higher than the temperature at which the reaction would come to

an end in 4 h, so as to complete the reaction. Completion of said reaction means that even when reaction is further carried out, there is substantially no change in the integrated intensity of the barium titanate-based semiconductor ceramic material powder in the X-ray diffraction pattern.

[0059]

Usually, the aging reaction is performed at a temperature in the range of 40-100°C, or preferably in the range of 60-100°C. The aging reaction is carried out under ambient pressure or under reduced pressure. For example, when the aging reaction is carried out under an elevated pressure in a sealed vessel, the obtained barium titanate-based semiconductor ceramic material powder is prone to becoming fine grains of 0.1 μm or smaller, or, although the grain size may be 0.3 μm or larger, the shape of the grains will not become spherical, and the grain size distribution will broaden. As a result, the spherical barium titanate-based semiconductor ceramic material powder with grain size of 0.3-5 μm cannot be obtained. This tendency is especially significant when reaction occurs under an elevated pressure at 100°C or higher.

[0060]

In addition, it is preferred that there be a nitrogen flow in the reaction system so as to prevent reaction between the barium compound and carbon dioxide component and other components in the air.

[0061]

The factors that will affect the particle size of the barium titanate semiconductor magnetic material powder in the aforementioned reaction will be described below.

[0062]

There is a tendency that as the concentration of the solution, especially the concentration of barium ions, is increased, the grain diameter becomes smaller.

[0063]

As far as Ba/Ti (atomic ratio) is concerned, the larger the ratio, the higher the concentration of the barium ions, and thus the smaller the grain diameter of the barium titanate-based semiconductor ceramic material powder.

[0064]

As far as the temperature of the reaction of the titanium compound and hydrogen peroxide is concerned, the higher the temperature, the smaller the grain diameter of the barium

titanate-based semiconductor ceramic material powder, and, the lower the temperature, the larger the grain diameter of the barium titanate-based semiconductor ceramic material powder.

[0065]

As far as the aging reaction temperature is concerned, when aging reaction is performed for a long time near the temperature at which reaction of the titanium compound and barium compound takes place and formation of barium titanate starts, the grain diameter becomes larger. Also, the higher the aging reaction temperature, the smaller the grain diameter.

[0066]

When barium titanate-based semiconductor ceramic material powder containing strontium is manufactured, while the proportion of barium is kept at 50 atom% or higher, the total proportion by atom of barium and strontium is the same as total proportion by atom of barium in the conventional case when barium is used alone.

[0067]

In addition, when a spherical barium titanate-based semiconductor ceramic material powder containing strontium is manufactured, since a strontium compound can react more easily than a barium compound, it is necessary to have the Sr/Ban atomic ratio during the reaction smaller than the Sr/Ban atomic ratio of the manufactured spherical barium titanate-based semiconductor ceramic material powder.

[0068]

Manufacturing of spherical barium titanate-based semiconductor ceramic material powder containing calcium (Ca) and lead (Pb) is carried out by adding calcium titanate (CaTiO_3) or lead titanate (PbTiO_3) with grain diameter of 0.2 μm or smaller beforehand to the wet reaction of the titanium compound and barium compound, or to the wet reaction of the titanium compound, barium compound, and strontium compound.

[0069]

For example, lead titanate in fine grain form may be manufactured using the method described in Japanese Kokai Patent Application No. Hei 3[1991]-80117. Also, it may be manufactured using the same method as that for calcium titanate.

[0070]

By adding fine grains with grain diameter of 0.2 μm or smaller of strontium titanate (SrTiO_3) to the wet reaction of the titanium compound and barium compound, it is possible to manufacture spherical barium titanate-based semiconductor ceramic material powder containing strontium.

[0071]

When spherical barium titanate-based semiconductor ceramic material powder containing calcium or lead is manufactured, or when fine grains are used for manufacturing spherical barium titanate-based semiconductor ceramic material powder containing strontium, the grain diameter of the added calcium titanate, lead titanate, strontium titanate, etc., should be 0.2 μm or smaller. This is because if the grain diameter is larger than 0.2 μm , it is difficult during baking to obtain spherical barium titanate-based semiconductor ceramic material powder with a uniform composition.

[0072]

For the obtained spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 0.3-5 μm , because the aggregates are strong, the aggregation state is not damaged in the conventional water washing, filtering, drying, baking, and other operations.

[0073]

As far as the final A/Ti (atomic ratio) after the wet reaction is concerned, by means of water washing or, as needed, pH adjustment using acetic acid or other acid, it is possible to adjust to the desired A/Ti (atomic ratio).

[0074]

Usually, it is preferred that A/Ti (atomic ratio) of the spherical barium titanate-based semiconductor ceramic material powder be adjusted to 0.98-1.02. If A/Ti (atomic ratio) is smaller than 0.98, when the barium titanate-based semiconductor ceramic material powder is molded and sintered to form ceramics, the obtained ceramics will not display semiconductor property. On the other hand, if A/Ti (atomic ratio) is larger than 1.02, although the semiconductor property is displayed, excessive barium will be present in the grain boundaries in the ceramics obtained by molding and sintering the barium titanate-based semiconductor ceramic material powder, and the resistivity versus temperature characteristics (PTC characteristics) will be lowered. In addition, when A/Ti (atomic ratio) is larger than 1.05, when the barium titanate-

based semiconductor ceramic material powder is molded and sintered to form ceramics, no semiconductor property will be displayed.

[0075]

When spherical barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 5-50 μm is to be formed, hydrogen peroxide is not added (hydrogen peroxide may be added) to said wet reaction in order to form primary grains with grain diameter of 0.2 μm or smaller and which are free of aggregates. Then, water washing and filtering are performed to adjust A/Ti (atomic ratio) to any value in the range of 0.98-1.02, followed by converting to a slurry again and then drying in a gas flow.

[0076]

For example, a rotary spraying-type spray dryer can be used as the method for drying in a gas flow. For the formed barium titanate-based semiconductor ceramic material powder with grain diameter in the range of 5-50 μm , a classification method or other method is used as needed to realize a sharp grain size distribution. When the method of drying in a gas flow is used, it is difficult to obtain a barium titanate-based semiconductor ceramic material powder with grain diameter of 5 μm or smaller.

[0077]

As explained above, the spherical barium titanate-based semiconductor ceramic material powder which contains a trivalent semiconductor-forming element or a pentavalent semiconductor-forming element in amount in the range of 0.05-2 atom% with respect to titanium, has the base material portion made of ATiO_3 and a grain diameter in the range of 0.3-50 μm .

[0078]

According to this invention, the grain diameter of spherical barium titanate-based semiconductor ceramic material powder should be in the range of 0.3-50 μm . This is due to the following reason. That is, when the grain diameter is smaller than 0.3 μm , the dispersion property in the binder during molding before formation of ceramics becomes poor, and a molding with a uniform composition cannot be obtained. Also, when the grain diameter is larger than 50 μm , when ceramics are formed, portions with grain size larger than 50 μm are formed, and the electrical characteristics and mechanical characteristics of the obtained semiconductor ceramics degrade.

[0079]

The spherical barium titanate-based semiconductor ceramic material powder of this invention literally has a spherical shape, a narrow grain size distribution, and excellent dispersion property. Consequently, when ceramics are formed, the desired grain size is realized, with little dispersion in the grain size, and it is thus possible to form PTC thermistors, semiconductor capacitors, and other semiconductor ceramics with conventional electrical characteristics and mechanical characteristics.

[0080]

As explained above, the spherical barium titanate-based semiconductor ceramic material powder of this invention can be used directly as a raw material in manufacturing PTC thermistors, semiconductor capacitors, and other semiconductor ceramics. However, when the barium titanate-based semiconductor ceramic material powder of this invention is baked, sintering becomes less, crystallinity becomes better, the grain diameter of the spherical barium titanate-based semiconductor ceramic material powder before baking can be maintained, the grain size distribution is narrow, and the dispersion property is good for the cubic-system spherical barium titanate-based semiconductor ceramic material powder or tetragonal-system spherical barium titanate-based semiconductor ceramic material powder obtained in this treatment.

[0081]

Baking of the spherical barium titanate-based semiconductor ceramic material powder of this invention may be carried out at a temperature in the range of 300-1350°C. However, in order to maintain the aforementioned spherical shape during baking, it is appropriate to bake it at a temperature in the range of 300-1200°C.

[0082]

By baking the spherical barium titanate-based semiconductor ceramic material powder of this invention at a temperature in the range of 1000-1200°C, it is possible to obtain a semiconductor powder maintaining its spherical shape. By using the obtained spherical semiconductor powder, it is possible to suppress the reaction of the sintering aid and the grain boundary component with the semiconductor-forming element or barium titanate, so as to obtain semiconductor ceramics with even higher performance.

[0083]

Compared with the barium titanate-based semiconductor ceramic material powder prepared using the conventional solid-phase method or wet method, the aforementioned spherical barium titanate-based semiconductor ceramic material powder has a narrower grain size distribution and has a better spherical shape. Consequently, in the molding operation, the amount of air carried with it becomes smaller, so that it can suppress generation of lamination. Compared with the barium titanate-based semiconductor ceramic material powder prepared using the conventional method, it is possible to obtain a molding with higher uniformity and higher density. Also, the final density of the sintered body can be significantly increased.

[0084]

Consequently, by using the aforementioned spherical barium titanate-based semiconductor ceramic material powder, it is possible to obtain PTC thermistors with uniform grain size and excellent resistivity versus temperature characteristics, and semiconductor capacitors with high dielectric constant and small dielectric loss.

[0085]

When the spherical barium titanate-based semiconductor ceramic material powder of this invention is baked at 900-1350°C, it is possible to obtain rectangular parallelepipedal barium titanate-based semiconductor ceramic material powder with each grain unit in a single crystal form.

[0086]

For said rectangular parallelepipedal barium titanate-based semiconductor ceramic material powder, too, because the spherical barium titanate-based semiconductor ceramic material powder before baking has a spherical shape, there is little sintering while baking. Consequently, the grain diameter before baking can almost [completely] be maintained, the grain size distribution is narrow, and the dispersion property is excellent.

[0087]

Because said rectangular parallelepipedal barium titanate-based semiconductor ceramic material powder is a barium titanate-based semiconductor ceramic material powder with a density higher than that of the aforementioned spherical barium titanate-based semiconductor ceramic material powder, precise control of the grain size and grain boundary for the semiconductor ceramics is easier. Consequently, the rectangular parallelepipedal barium titanate-based semiconductor ceramic material powder can be used easily in manufacturing PTC

thermistors with low room-temperature resistivity and high resistance variation rate, and semiconductor capacitors with high dielectric constant, low dielectric loss, and good voltage rating.

[0088]

Effect of the invention

For the spherical barium titanate-based semiconductor ceramic material powder of this invention, the grain diameter can be controlled as desired. The grain size distribution is narrow, the shape is spherical, and the dispersion property is excellent.

[0089]

Consequently, the spherical barium titanate-based semiconductor ceramic material powder of this invention can be used in manufacturing PTC thermistors, semiconductor capacitors, and other semiconductor ceramics with desired grain size, little dispersion in grain size, and excellent electrical characteristics and mechanical characteristics.

[0090]

By baking the spherical barium titanate-based semiconductor ceramic material powder of this invention, it is possible to obtain a cubic-system barium titanate-based semiconductor ceramic material powder or tetragonal-system spherical barium titanate-based semiconductor ceramic material powder with little sintering, with the grain diameter of the spherical barium titanate-based semiconductor ceramic material powder before baking almost [completely] maintained, and having narrow grain size distribution and excellent dispersion property.

[0091]

Said cubic-system barium titanate-based semiconductor ceramic material powder or tetragonal-system spherical barium titanate-based semiconductor ceramic material powder can be used in manufacturing PTC thermistors and semiconductor capacitors with good crystallinity, better controlled grain size and grain boundary, and other excellent properties.

[0092]

By baking the spherical barium titanate-based semiconductor ceramic material powder of this invention at a high temperature, it is possible to obtain a single-crystal rectangular parallelepipedal barium titanate-based semiconductor ceramic material powder with little sintering and a narrow grain size distribution.

[0093]

Because said rectangular parallelepiped barium titanate-based semiconductor ceramic material powder is a barium titanate-based semiconductor ceramic material powder with a density higher than that of the aforementioned spherical barium titanate-based semiconductor ceramic material powder, precise control of the grain size and grain boundary for the semiconductor ceramics is easier. Consequently, the rectangular parallelepiped barium titanate-based semiconductor ceramic material powder can be used in manufacturing PTC thermistors, semiconductor capacitors, etc., with even better characteristics.

[0094]

Application examples

In the following, this invention will be explained in more detail with reference to application examples.

[0095]

Application Example 1

By means of a 15% aqueous ammonia solution, an aqueous solution of titanium tetrachloride containing yttrium was hydrolyzed by adding yttrium nitrate in an appropriate amount so that the amount of yttrium with respect to titanium is 0.3 atom% (product of Osaka Titanium Co., Ltd., with content of titanium of 16.4 %). The obtained gel-like product was filtered and washed with water, forming titanium hydroxide cake (I) with equivalent concentration of titanium oxide by weight of 12.3% according to ignition loss, and containing 0.3 atom% of yttrium.

[0096]

81 g of 30% hydrogen peroxide were added to a suspension prepared by uniformly dispersing 72 g of said titanium hydroxide cake (I) containing 0.3 atom% of yttrium in 380 g of water. In this case, the molar ratio of hydrogen peroxide to titanium oxide (hereinafter referred to as " $\text{H}_2\text{O}_2/\text{TiO}_2$ (molar ratio)") is 6.35. The concentration of titanium oxide in the obtained slurry is 0.225 mol/L with calculation made assuming 70% of said 30% aqueous hydrogen peroxide solution is water.

[0097]

The obtained slurry was slowly heated with stirring, and reflux was performed at 100°C for 2 h to form a suspension solution (II). This suspension solution (II) was cooled naturally to 40°C. Then, nitrogen gas was blown in to purge the air. Then, 56.8 g of barium hydroxide

octahydrate (Ba/Ti (atomic ratio) = 1.6) were added to said suspension solution (II), followed by heating from 30°C to 70°C over 0.25 h, and then aging reaction at 70°C for 3 h, and finally refluxing at 100°C for 4 h to complete the reaction.

[0098]

For the barium titanate-based semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured above, electron microscopy indicated that it is spherical grains with grain diameter at 90% number distribution of 1.2-1.4 μm , and it has a narrow grain size distribution and an average grain diameter of 1.3 μm .

[0099]

Figure 1 is an electron microgram (magnification of 15,000X) illustrating the grain structure of the spherical barium titanate-based semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 1. As can be seen from Figure 1, for the spherical barium titanate-based semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 1, the spherical shape of the grains is still maintained even after magnification of 15,000X. Also, the grain diameter is nearly uniform, and the grain size distribution is narrow.

[0100]

Application Example 2

By means of 15% aqueous ammonia solution, an aqueous solution of titanium tetrachloride containing antimony was hydrolyzed by adding antimony pentachloride in an appropriate amount so that the amount of antimony with respect to titanium is 0.25 atom%. The obtained gel-like product was filtered and washed with water, forming a titanium hydroxide cake with equivalent concentration of titanium oxide by weight of 24.5% according to ignition loss, and containing 0.25 atom% of antimony.

[0101]

112.5 g of 30% hydrogen peroxide were added to a suspension prepared by uniformly dispersing 51.7 g of said titanium hydroxide cake containing 0.25 atom% of antimony in 382 g of water ($\text{H}_2\text{O}_2/\text{TiO}_2$ (molar ratio) = 6.26), forming a slurry with concentration of titanium oxide of 0.312 mol/L.

[0102]

The obtained was heated with reflux at 100°C for 2 h to form a suspension solution. This suspension solution was cooled naturally to 40°C. Then, 69 g of barium hydroxide octahydrate (Ba/Ti (atomic ratio) = 1.4) were added to said suspension solution (II), followed by aging reaction at 70°C for 3 h, and finally refluxing at 100°C for 4 h to complete the reaction.

[0103]

For the barium titanate-based semiconductor ceramic material powder containing 0.25 atom% of antimony manufactured above, electron microscopy indicated that it is spherical grains with grain diameter at 90% number distribution of 0.6-0.8 μm , and it has a narrow grain size distribution and an average grain diameter of 0.7 μm .

[0104]

After said spherical grains obtained above were pickled with acetic acid, and Ba/Ti (atomic ratio) was adjusted to 1.014, it was baked at 1100°C. As a result, a semiconductor powder maintaining its spherical shape was obtained.

[0105]

Application Example 3

Using the following methods, strontium titanate, calcium titanate, and lead titanate were manufactured. They were added during the manufacturing of the barium titanate-based semiconductor ceramic material powder containing yttrium just as in Application Example 1, forming yttrium-containing barium strontium calcium lead titanate-based semiconductor ceramic material powder.

[0106]

Manufacturing of strontium titanate

1 kg of an aqueous solution of titanium tetrachloride (16% of titanium in aqueous solution) was added to 23 L of distilled water with stirring. Then, 5% aqueous ammonia solution was added for hydrolysis, with pH 8, followed by filtering and water washing. The obtained titanium hydroxide gel was converted to a slurry with content of titanium oxide of 5%. After heating to 60°C, acetic acid was added to adjust the pH to 6. While said pH and temperature were maintained, agitation was performed for 1 h. The obtained slurry was filtered and washed with water, forming titanium hydroxide gel with concentration of titanium oxide of 10.3% equivalent weight according to ignition loss.

[0107]

300 g of distilled water were added to 777 g (1 mol in titanium oxide equivalent) of titanium hydroxide gel with concentration of titanium oxide of 10.3%, and the mixture was agitated in a nitrogen atmosphere, followed by heating to 80°C, forming a titanium oxide slurry.

[0108]

In a nitrogen atmosphere, strontium hydroxide was dissolved to form 1 L of an aqueous solution containing 10.5% of strontium component (containing 1.2 mol of strontium). It was heated to 80°C. With atomic ratio of strontium to titanium (Sr/Ti (atomic ratio)) of 1.2, said titanium oxide slurry and aqueous strontium solution were added simultaneously while being kept under a nitrogen atmosphere at 80°C, followed by agitation for 2 h to perform reaction.

[0109]

Then, after heating to a temperature of 100°C or higher, and agitation for 1 h, filtering and water washing were performed. The obtained strontium titanate is uniform fine grains with grain diameter in the range of 0.02-0.04 µm.

[0110]

Manufacturing of calcium titanate

100.09 g of commercially available calcium carbonate were crushed to grains with grain diameter of 0.1 µm or smaller using a ball mill. Then, 79.9 g of titanium oxide (rutile type, grain diameter of 0.1 µm) were added, and the mixture was further crushed and mixed for 2 h, followed by spray drying using a spray drier. It was baked (reacted) at 1000°C for 2 h, forming calcium titanate with grain diameter of 0.2 µm.

[0111]

Manufacturing of lead titanate

292 g (1 mol in equivalent of titanium oxide) of aqueous titanium tetrachloride solution (product of Osaka Titanium Co., Ltd., with titanium content in the aqueous solution of 16%, and chlorine content of 32%) were loaded in a beaker. Water was added to 1 L. Then, the aqueous solution was added dropwise slowly to 1 L of 9% aqueous ammonia solution. The obtained white slurry was filtered and washed with water, forming a titanium hydroxide cake. It was loaded in a platpot [transliteration]. Then, 223 g (1 mol) of commercially available lead monoxide and 3 kg of 5-mm-diameter yttria-stabilized zirconia balls were added, followed by addition of 1 L of water. The system was then sealed, and ball milling was carried out for 3 h.

[0112]

Zirconia balls were removed from the obtained slurry and the obtained slurry was sprayed and dried using a spray drier. The obtained powder was dried at 100°C for 12 h, forming a precursor substance of lead titanate (grain diameter of 0.2 μm). It was then baked at 490°C for 5 h, forming nearly uniform fine grains of lead titanate with grain diameter of 0.1 μm .

[0113]

Manufacturing of spherical barium strontium calcium lead titanate semiconductor ceramic material powder containing yttrium

[0114]

In the same way as in Application Example 1, aqueous hydrogen peroxide solution was added to titanium hydroxide cake (I) containing 0.3 atom% yttrium prepared in Application Example 1, followed by the same treatment, forming suspension solution (II) just as in Application Example 1.

[0115]

After said suspension solution (II) was cooled to 40°C or lower, nitrogen gas was blown in to purge the air. Then, said manufactured strontium titanate (with grain diameter in the range of 0.02-0.04 μm), calcium titanate (grain diameter of 0.2 μm), and lead titanate (grain diameter of 0.1 μm) were added with molar ratio of strontium titanate, calcium titanate and lead titanate of $\text{TiO}_2\text{:SrTiO}_3\text{:CaTiO}_3\text{:PbTiO}_3 = 80\text{:}9\text{:}4\text{:}7$, and the mixture was blended homogeneously.

[0116]

Then, barium hydroxide octahydrate (Ba/Ti (atomic ratio) = 1.6) was added to said slurry, and, just as in Application Example 1, the mixture was heated from 30°C to 70°C over 0.25 h, and then aging reaction was performed at 70°C for 3 h, followed by refluxing at 100°C for 4 h.

[0117]

The obtained reaction mixture was filtered and washed with water, followed by adding acetic acid to adjust to $(\text{Ba} + \text{Sr} + \text{Ca} + \text{Pb})/\text{Ti}$ (atomic ratio) = 0.994.

[0118]

The obtained barium strontium calcium lead titanate semiconductor ceramic material powder containing 0.3 atom% yttrium was analyzed using a fluorescent X-ray analyzer, and the composition except for the yttrium component was found to be $(\text{Ba}_{0.80} \text{Sr}_{0.09} \text{Ca}_{0.04} \text{Pb}_{0.07} \text{TiO}_3)$.

Electron microscopy indicated that the grain diameter at 90% number distribution is 0.4-0.6 μm , and it has a narrow grain size distribution and an average grain diameter of 0.5 μm .

[0119]

Figure 2 is an electron microgram (magnification of 15,000X) illustrating the grain structure of the spherical barium strontium calcium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 3. As can be seen from Figure 2, for the spherical barium strontium calcium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 3, the spherical shape of the grains is still maintained even after magnification of 15,000X. The grain diameter is nearly uniform, and the grain size distribution is narrow.

[0120]

Application Example 4

A slurry (containing 8% of titanium oxide) prepared by adding 1040 g of water to 2390 g of titanium hydroxide cake (I) containing 0.3% of yttrium prepared in Application Example 1 (containing 0.38 mol of titanium component), followed by boiling the mixture, and 9710 g (containing 1.7 mol of barium component) of 30% aqueous barium hydroxide solution prepared under a nitrogen atmosphere and boiled, were kept at 100°C as they were fed through an in-line mixer to be mixed with each other, followed by heating with reflux in 4 h for reaction.

[0121]

The slurry obtained from the reaction was filtered, rinsed to obtain crystalline barium containing 0- . Atom% of yttrium with a particle size of 0.01 μm or less.

[0122]

After reaction, acetic acid was added to the crystalline barium titanate containing 0.3 atom% of yttrium for pickling. Then, 100 g of crystalline barium titanate containing 0.3 atom% of yttrium with Ba/Ti (atomic ratio) adjusted to 0.992, 9.59 g of strontium titanate prepared using the manufacturing method described in Application Example 3, and 12.68 g of lead titanate were added, and the mixture was uniformly mixed in a ball mill. Then, a spray drier manufactured by Ogawahara Kakoki K.K. was used for spraying drying and pelletization. After baking at 800°C for 2 h, wet classification was performed using a 500-mesh sieve and a 325-mesh sieve, forming grains with grain diameter of 30-45 μm .

[0123]

The obtained grains were baked at 800°C for 2 h in a sealed vessel, forming a powder with a relatively uniform grain diameter of 37 μm and good dispersion property.

[0124]

For the obtained powder, quantitative determination was performed by fluorescent X-ray. It was found that for the barium strontium lead titanate containing 0.3 atom% of yttrium, the composition except for the yttrium component of $(\text{Ba}_{0.82} \text{Sr}_{0.10} \text{Pb}_{0.08}) \text{TiO}_3$.

[0125]

Figure 3 is an electron microgram (magnification of 900X) illustrating the grain structure of the spherical barium strontium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 4. As can be seen from Figure 3, for the spherical barium strontium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 4, the spherical shape of the grains is still maintained even after magnification of 900X. The grain diameter is nearly uniform, and the grain size distribution is narrow.

[0126]

Application Example 5

81 g of 30% hydrogen peroxide were added to a suspension solution prepared by uniformly dispersing, in 380 g water, 72 g of titanium hydroxide cake (I) containing 0.3 atom% of yttrium prepared in Application Example 1. In this case, the molar ratio of hydrogen peroxide to titanium oxide ($\text{H}_2\text{O}_2/\text{TiO}_2$ (molar ratio)) is 6.35, and the concentration of titanium oxide in the obtained slurry is 0.225 mL/L.

[0127]

While the obtained slurry was agitated, it was heated slowly, and refluxing at 100°C was performed for 2 h, forming a suspension solution. After the suspension solution was cooled to 40°C or lower, nitrogen gas was blown in to replace air. Then, 51.10 g of barium hydroxide octahydrate and 10.76 g of strontium hydroxide octahydrate were added to said suspension solution such that the molar ratio of barium hydroxide and strontium hydroxide was 8:2. The mixture was heated from 30°C to 70°C over 0.25 h, and aging reaction was performed at 70°C for 3 h, followed by refluxing at 100°C for 4 h to complete the reaction. In the reaction, the atomic ratio of $(\text{Ba}+\text{Sr})/\text{Ti}$ is 1.8.

[0128]

For the barium strontium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in said reaction, Ba/Sr (atomic ratio) is 7/3. The proportion of strontium is increased. As shown in Figure 4, for the obtained barium strontium semiconductor ceramic material powder containing 0.3 atom% of yttrium, the grains have a grain diameter of about 0.4 μm , and have a spherical shape.

[0129]

From the aforementioned results, it can be seen that in manufacturing of barium strontium titanate, strontium reacts with priority. Consequently, this fact is taken into consideration in determining the amount of strontium to be added for the desired ratio of Ba/Sr.

[0130]

Application Example 6

A slurry (containing 1.8% of titanium oxide) prepared by adding water to titanium hydroxide cake (I) containing 0.3 atom% of yttrium prepared in Application Example 1, followed by uniformly blending the mixture, and barium hydroxide octahydrate were mixed with each other with atomic ratio of Ba/Ti of 1.2, followed by heating with reflux at 100°C for 4 h for reaction.

[0131]

The obtained slurry was filtered, washed with water, and pickled with acetic acid, followed by baking at 800°C for 2 h, forming spherical barium titanate grains containing 0.3 atom% of yttrium with Ba/Ti (atomic ratio) of 0.992 and with grain diameter of 0.1 μm .

[0132]

In an operation separated from the aforementioned operation, aggregate grains of barium titanate containing 0.3 atom% of yttrium with grain diameter of 1.2-1.4 μm prepared in Application Example 1 were subjected to the same pickling treatment as above to adjust the ratio of Ba/Ti (atomic ratio) to 0.992, followed by baking at 1000°C for 2 h, forming spherical barium titanate containing 0.3 atom% of yttrium with grain diameter in the range of 1.2-1.4 μm .

[0133]

Said barium titanate grains containing 0.3 atom% of yttrium and with grain diameter of 0.1 μm and barium titanate grains containing 0.3 atom% of yttrium and with grain diameter of 1.2-1.4 μm were mixed homogeneously with each other at a ratio by weight of 3:7. Then,

0.04 mol% of manganese nitrate and 0.15 mol% of fine grains of silicon dioxide were added to the mixture, followed by blending using a ball mill. Then, 0.4 wt% of polyvinyl alcohol as a binder and 0.4 wt% of polyethylene glycol as a deflocculating agent were added to the mixture, followed by spray drying using a spray drier, and pelletization to form grains with grain diameter of 30 μm .

[0134]

The obtained grains were loaded in a molding die, then pressed under a pressure of 1 t/cm² to form a 15-mm-diameter cylindrical body, followed by sintering at 1250°C to form a semiconductor ceramic body. For the obtained semiconductor ceramic body, the grain size (grain diameter) is nearly uniform and is 2-4 μm .

[0135]

Figure 7 is a diagram illustrating the resistivity versus temperature characteristics of the obtained ceramic body. Figure 7 will be explained in detail after Comparative Example 2.

[0136]

Comparative Example 1

In Comparative Example 1, barium titanate containing 0.22 atom% of niobium was manufactured using the solid-phase method. There is clearly a dispersion in the grain shape and grain diameter.

[0137]

98.66 g of commercially available barium carbonate, 40.34 g of titanium oxide, and 0.1462 g of niobium pentoxide were homogeneously blended using a ball mill for 30 min, followed by spray drying using a spray drier. The obtained powder was subject to primary molding under a pressure of 300 kg/cm², and then baking at 1150°C for 2 h, forming a barium titanate semiconductor ceramic material powder containing 0.22 atom% of niobium.

[0138]

Figure 5 shows the electron microgram (magnification of 10,000X) of the obtained barium titanate semiconductor ceramic material powder containing 0.22 atom% of niobium.

[0139]

As can be seen from Figure 5, for the barium titanate containing 0.22 atom% of niobium prepared using the solid-phase method, the grain shape is nonuniform, and the dispersion in the grain diameter is significant.

[0140]

Comparative Example 2

In Comparative Example 2, barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium was manufactured using the wet method. There is clearly a dispersion in the grain shape and grain diameter.

[0141]

Under a flow of nitrogen gas, 390 g of a slurry of titanium hydroxide cake (I) containing 0.3 atom% of yttrium (with concentration of titanium oxide of 22.8% in the equivalent weight by means of ignition loss) prepared using the same method as in Application Example 1 were heated to 60°C, and 428 g of barium hydroxide octahydrate (Ba/Ti (atomic ratio) = 1.2) were added, and the mixture was agitated to form a uniform slurry.

[0142]

The slurry was further heated with reflux at 100°C for 4 h (feeding of nitrogen gas was stopped during heating). After filtering and water washing, spray drying was performed with a spray drier, forming barium titanate powder containing 0.3 atom% of yttrium. In the reaction, Ba/Ti (atomic ratio) is 1.2.

[0143]

After the obtained barium titanate powder containing 0.3 atom% of yttrium was baked at 800°C for 5 h, pickling treatment was performed with acetic acid to adjust Ba/Ti (atomic ratio) to 0.992 to form a semiconductor material.

[0144]

After pickling treatment, the barium titanate powder containing 0.3 atom% of yttrium (Ba/Ti (atomic ratio) = 0.992) was baked again at 800°C for 2 h, forming grains with uniform grain diameter of 0.03-0.06 μm .

[0145]

However, when the same pickled powder was baked at 1200°C for 3 h, the grain diameter became as large as 0.06-1 μm , and the grain shape became irregular as shown in Figure 6 (Figure 6 is an electron microgram with magnification of 15,000X).

[0146]

Then, said powder baked at 800°C and powder baked at 1200°C having different grain diameters were mixed at a ratio by weight of 3:7. Then, 0.04 mol% of manganese nitrate and 0.15 mol% of fine grains of silicon dioxide were added, and the mixture was blended with a ball mill. Then, 0.4 wt% of polyvinyl alcohol as a binder and 0.4 wt% of polyethylene glycol as a deflocculating agent were added to the mixture, followed by spray drying using a spray drier, and pelletization to form grains.

[0147]

The obtained grains were loaded in a molding die, then pressed under a pressure of 1 t/cm² to form a 15-mm-diameter cylindrical body, followed by sintering at 1250°C to form a semiconductor ceramic body. For the obtained semiconductor ceramic body, the grain size (grain diameter) is nearly uniform and is 5-10 μm .

[0148]

Figure 7 is a diagram illustrating the resistivity versus temperature characteristics of the obtained ceramic body.

[0149]

In Figure 7, curve a shows the resistivity versus temperature characteristics of the semiconductor ceramic body prepared from spherical barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured according to Application Example 6 of this invention. Curve b shows the resistivity versus temperature characteristics of the semiconductor ceramic body prepared from the barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured using the wet method in said Comparative Example 2.

[0150]

As can be seen from curve a and curve b (comparative example) in Figure 7, compared with the semiconductor ceramic body prepared from the barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured using the wet method in said

Comparative Example 2, for the semiconductor ceramic body prepared from spherical barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured according to Application Example 6 of this invention, the resistivity at room temperature is lower, and variation in resistance is wider.

Brief description of the figures

Figure 1 shows an electron microgram with magnification of 15,000X illustrating the grain structure of the spherical barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 1.

Figure 2 shows an electron microgram with magnification of 15,000X illustrating the grain structure of the spherical barium strontium calcium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 3.

Figure 3 shows an electron microgram with magnification of 900X illustrating the grain structure of the spherical barium strontium lead titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 4.

Figure 4 shows an electron microgram with magnification of 15,000X illustrating the grain structure of the spherical barium strontium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 5.

Figure 5 shows an electron microgram with magnification of 10,000X illustrating the grain structure of the barium titanate semiconductor ceramic material powder containing 0.22 atom% of niobium manufactured using the solid-phase method in Comparative Example 1.

Figure 6 shows an electron microgram with magnification of 15,000X illustrating the grain structure of the barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured using the wet method in Comparative Example 2.

Figure 7 is a diagram illustrating the resistivity versus temperature characteristics of the semiconductor ceramic body prepared from the spherical barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured in Application Example 6, and the resistivity versus temperature characteristics of the semiconductor ceramic body prepared from the barium titanate semiconductor ceramic material powder containing 0.3 atom% of yttrium manufactured using the wet method in Comparative Example 2.

[Amendment 1]\\

[Amendment]

[Amendment date] July 20, 1993

[Amendment 1]

[Amendment object document name]: Figures

[Amendment object item name]: Figure 1

[Amendment content]



Figure 1. Photograph used as substitution for figure

[Amendment 2]

[Amendment object document name]: Figures

[Amendment object item name]: Figure 2

[Amendment content]

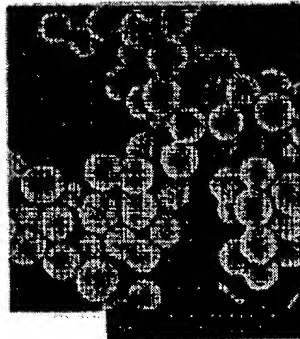


Figure 2. Photograph used as substitution for figure

[Amendment 3]

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[Amendment object item name]: Figure 3

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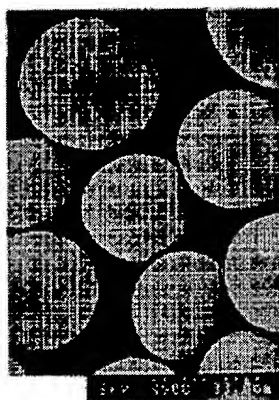


Figure 3. Photograph used as substitution for figure

[Amendment 4]

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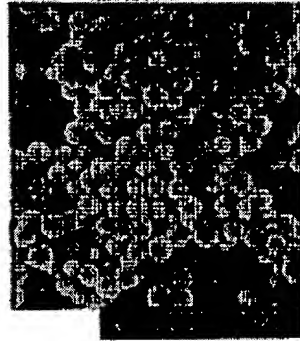


Figure 4. Photograph used as substitution for figure

[Amendment 5]

[Amendment object document name]: Figures

[Amendment object item name]: Figure 5

[Amendment content]



Figure 5. Photograph used as substitution for figure

[Amendment 6]

[Amendment object document name]: Figures

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[Amendment content]



Figure 6. Photograph used as substitution for figure

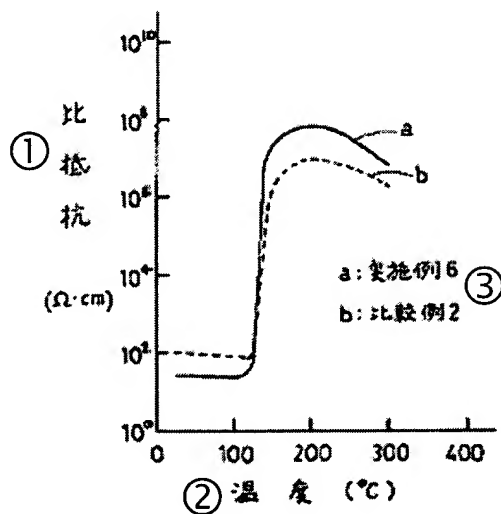


Figure 7

Key: 1 Resistivity
 2 Temperature
 3 a. Application Example 6
 b. Comparative Example 2